



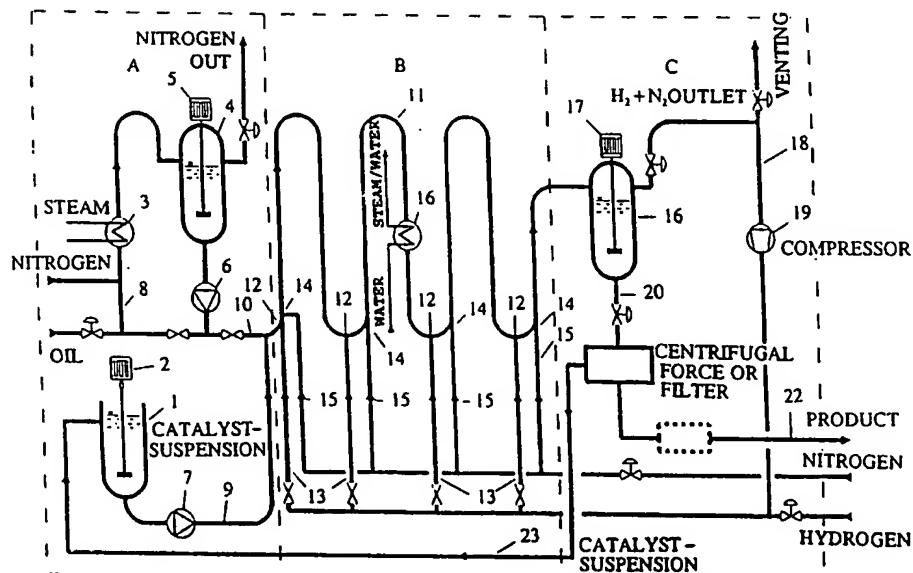
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/NO93/00167 (22) International Filing Date: 11 November 1993 (11.11.93) (30) Priority data: 924356                      12 November 1992 (12.11.92) NO (71) Applicant (for all designated States except US): NORSK HYDRO A.S [NO/NO]; N-0240 Oslo (NO). (72) Inventor; and (75) Inventor/Applicant (for US only) : HENRIKSEN, Norolf [NO/NO]; Rugdeveien 9, N-3670 Notodden (NO). (74) Agent: HOFSETH, Svein; Norsk Hydro a.s., N-0240 Oslo (NO).	(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.	

(54) Title: METHOD AND EQUIPMENT FOR HARDENING OIL, FAT AND FATTY ACIDS

## (57) Abstract

A procedure and equipment for hydrogenating oil, fat or fatty acids by adding hydrogen and using a catalyst. The procedure consists in a semi-continuous or continuous process in which the catalyst is mixed with pre-heated fat or oil in a mixing device (9/10, 24), the mixture is fed through a preferably serpentine-like, vertically-mounted pipe loop or one or more static mixers (11, 28) while hydrogen and, possibly, an inert gas is/are added so that a turbulent co-current is achieved, the mixture is cooled during the hydrogenation and, possibly, the oil, the catalyst, the inert gas and excess hydrogen gas are recirculated after the hardening process. The equipment comprises feed and mixing devices (A) for feeding and mixing oil and a catalyst, a preferably serpentine-like, vertically-mounted pipe loop or one or more static mixers and cooling devices with feed devices for the hydrogen gas and any inert gas (B), as well as devices (C) for collecting the oil, separating and recirculating any inert gas and feeding, separating and, possibly, recirculating used hydrogen gas, as well as separation and recirculation of the catalyst.



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Method and equipment for hardening oil, fat and fatty acids

The present invention concerns a method and equipment for hydrogenating or hardening oil, fat and fatty acids by adding hydrogen and using a catalyst.

In an existing method for hardening and stabilising oil, fat or fatty acids, a large, closed tank or container with a stirring device is used. The oil or fat is treated in batches by adding hydrogen in an eddy current which is created by a mechanical stirrer designed as a rotor with several sets of propeller blades or as a screw.

It is obvious that the hydrogenation efficiency of such a system is very low because the contact area between the gas, liquid and catalyst is small and the turbulence is poor.

This is also confirmed by the results obtained in practice where the reaction speed defined as the iodine reduction ( $\Delta I$ ) per time unit is low, for example 0.3  $\Delta I$ /min.

With a low reaction speed large, space-consuming and costly processing equipment is required to obtain the desired processing capacity. Another fundamental weakness of batch systems is that the consumption of hydrogen is very irregular. In the first phase of the process the consumption of hydrogen is high but goes down radically as the proportion of unsaturated molecules in the oil batch becomes low.

In some cases the consumption of hydrogen in the first half hour can be approximately 80 % of the total consumption, while it can take 4-6 hours for the hydrogenation to be completed.

Other disadvantages are that it is difficult to control the process in a large autoclave where temperature differences and different hardening processes from place to place in the autoclave will occur. The energy consumption for mechanical stirring will also be relatively high and optimal stirring can usually not be justified on account of the energy consumption.

Equipment of the above, existing type is discussed in more detail in the publication INFORM, Vol. 3, No. 7, July 1992.

Another existing system of the batch type is the Sullivan system (Alfa-Laval). Generally speaking, it works in the same way as the above system, but a higher reaction speed is obtained by recirculating the hydrogen which flows to the top of the autoclave by means of a compressor through a perforated ring back to the base of the tank.

The reaction speed in the Sullivan system is stated as 1.5 - 2  $\Delta$  I/min., but apart from this improvement the weaknesses of the system are the same as for the conventional batch process.

It has therefore been an aim of the present invention to create a solution for hardening or hydrogenating fat or oil which is, in its entirety, considerably more efficient than existing solutions.

The aim has been to achieve

- higher reaction speed
- regular hydrogen consumption
- simple, reliable process control
- selective hydrogenation
- low catalyst consumption
- reduction of energy consumption (kW).

In accordance with the present invention the stated objectives were achieved by a procedure for hardening oil or fat which is characterised by a semi-continuous or continuous process in which the catalyst is mixed with preheated fat or oil in a mixing device, whereby the mixture is passed through a preferably serpentine-like, vertically-mounted pipe loop or one or more static mixers for the addition of hydrogen and, possibly, inert gas so that a turbulent co-current flow is achieved, the mixture is cooled during hydrogenation and, possibly, the oil, catalyst, inert gas and excess hydrogen gas are recirculated after the hardening process.

Furthermore, the present invention comprises processing equipment for the hardening of oil or fat which is characterised by feed and mixing devices for the addition and mixing of oil and a catalyst, a preferably serpentine-like, vertically-mounted pipe loop, or one or more static mixers and cooling devices with feed devices for hydrogen gas and, possibly, inert gas, and devices for collecting the oil, separating and recirculating any inert gas and the supply, separation and, possibly, recirculation of used hydrogen gas, as well as a possible separation and recirculation of the catalyst.

The dependent claims 2-3 and 5-12 define the advantageous features of the present invention.

The present invention shall now be defined in further detail by means of examples and with reference to the attached drawings in which Fig. 5 shows a continuous process equipment for the hardening or hydrogenation of oil or fat and Fig. 2 shows alternative equipment which, for example, can be used as a retrofit in existing hydrogenation systems. The equipment comprises, as Fig. 1 shows, a feed and mixing device A), a serpentine-like pipe loop B), and devices C) for separating and recirculating a catalyst, supply and recirculation of any inert gas, and supply and recirculation of any excess hydrogen gas. The feed and mixing device A) consists of a holding and recirculation tank 1 with a stirring device 2 for catalyst suspension, a heat exchanger 3 and a feed and stirring tank 4 for the oil or fat, and pumps 6, 7 with appropriate pipes 9, 10 for the transportation of the oil and the catalyst suspension respectively to a mixing point 10 where the pipes 8, 9 meet. The catalyst is preferably of Ni, deposited on carriers of minerals or plastics in the form of grain-like particles and the purpose of the stirring device 2 in the tank 1 is to keep this suspension homogeneous and prevent the deposition of catalyst particles on the base of the tank. In a similar way another purpose of the stirring device 5 is to keep a regular temperature in the oil or fat in the tank 4.

The oil, fat or fatty acid, depending on what is to be hardened, is fed from a storage tank or similar (not shown) via pipes 8, first through a heat exchanger 3, where it is heated, and subsequently to the stirring tank 4. From tank 4 the oil can be recirculated through the heat exchanger 3 by means of the pump 6. During the hydrogenation process the oil is pumped from tank 4 on to the mixing point 10 where it is mixed with the catalyst suspension from the holding tank 1. From here the mixture is transported through a serpentine-like pipe loop 11 into the hydrogenation system B). Hydrogen in the quantities required is supplied to the pipe loop 11 at several points 12 via supply pipes 13 and flows with the oil in a turbulent co-current (bubble-flow), at the same time as the reaction with the oil takes place.

In a corresponding manner any inert gas, for example nitrogen, is added at different points 14 via supply pipes 15.

The addition of any inert gas is intended to regulate the hydrogen cover of the catalyst and thereby control the reaction speed and obtain selective hydrogenation, at the same time as maintaining the turbulent gas-liquid current.

Moreover, one or more coolers or heat exchangers 21 are mounted in the pipe loop. The purpose of these is to gradually remove the heat generated during the exothermic hardening process and keep the optimum reaction temperature. This heat can be expediently used to preheat untreated oil which is to be fed into part A) of the processing system. This produces a considerable reduction in energy consumption.

From the pipe loop, the oil, catalyst and gas mixture goes to part C) of the processing system, which comprises a collection tank 16 with a stirring device 17, a pipe system 18 with a compressor 19 for recirculating the excess inert and hydrogen gas, as well as a pipe system 20, possibly with a centrifuge and/or filter or similar built in to separate and recirculate the catalyst slurry.

The purpose of the stirring device 17 in the collection tank 16 is to prevent the catalyst being deposited on the base. Otherwise, the collection tank works like a gas separator and the collected gas is extracted from the top of the tank by means of the compressor 19. In this connection it should be noted that the gas which is extracted from the tank 16 may, depending on the reaction process, be pure inert gas or a mixture of inert gas and hydrogen and this gas is mixed with hydrogen from the hydrogen supply (not shown) via the pipe 18. The gas which is supplied to the pipe loop 11 through points 12 is thus a mixture of hydrogen and inert gas and the mixture ratio may, as stated earlier, be regulated in a precise manner to obtain the desired hardening speed and degree of hardening.

The oil/catalyst mixture is fed from the base of the tank 16 and, possibly, through a centrifuge or similar. The hardened oil is fed to a storage tank (not shown) via the pipe 22 while the catalyst is fed back to the holding tank 1 via the pipe 23.

Otherwise regarding Fig. 1 it should be noted that the present invention as it is described in the claims is not limited to the this solution. Thus the equipment shown may be used without the use of inert gas.

Furthermore, instead of two separate tanks 1 and 4, a joint tank for the catalyst and oil may be used, whereby the catalyst is recirculated to tank 4 instead of tank 1. Moreover, it may be practical to not recirculate the catalyst after hydrogenation but to have it discharged through the outlet pipe 22 together with the oil for later separation.

Fig. 2 shows an alternative processing system in accordance with the present invention which can easily be used for converting conventional batch systems but which can also be used for new systems. This solution can be described as semi-continuous as the oil is fed into the autoclave or container 24 in batches while the actual hydrogenation takes place continuously.

More precisely, Fig. 2 shows a large, closed container 24 which is designed to contain a certain quantity of oil plus a calculated quantity of catalyst, preferably Ni catalyst. A base stirrer ensures that the catalyst, which is mainly in the oil in the lower part of the container, is kept in suspension and is not deposited on the base of the container. The oil mixed with the catalyst is pumped out of the tank by means of a pump 26 via a pipe system 27 through a serpentine pipe system as described for the continuous hydrogenation system or through a set of static mixers/heat exchangers back to the top of the tank and out into it via a diffuser 29 which slows the speed and distributes the oil/gas flow.

The hydrogenation takes place in exactly the same way as with a continuous system such as that described earlier. Excess hydrogen and inert gas are extracted from the top of the tank and recirculated as in the continuous system. In the system shown in Fig. 2 the tank has no built-in heating device.

When the hardening process is to be set in train, the heat exchangers in the combined static mixer/heat exchanger are used to heat up the oil in the container but as soon as the temperature is sufficiently high (about 160°C) and the hardening process has started, the heat exchangers are used to cool the oil. Reference numbers 32 and 33 show, respectively, the inlet and the outlet for the heat exchanger's heat exchange medium which may be steam during heating and may be water during cooling.

During the hardening process the catalyst particles will sink towards the base in such a way that the catalyst concentration will be highest in the area where the stirring takes place. Moreover, the stirring is concentrated in the base volume so that it does not affect the oil above (above the dotted line). This means that the hardened oil which is returned to the container through the diffuser 29 will sink relatively quickly towards the base. In this way it will be possible to use a much smaller catalyst charge than with conventional batch systems.



When the hardening process has been completed, the oil can be pumped out and the container emptied through the discharge pipe 34. New, unhardened oil and catalyst are added to the container through the filling pipes 35, 36.

In the two previous examples, Fig. 1 and Fig. 2, a serpentine-like pipe loop and static mixers were used respectively. The present invention is, however, not limited to these two examples as, instead of a pipe loop as shown in Fig. 1, static mixers may be used and, instead of the static mixers shown in Fig. 2, a pipe loop with separately arranged heat exchangers may be used.

The length of the pipe loop or the number and length of the static mixers and heat exchangers can be adapted to the hydrogenation process to give optimal operating conditions.

The two examples shown are thus alternatives which are kept at the desired temperature by means of built-in heat exchangers/coolers in the loop 8.

#### Example

180 l refined soya oil was treated in a small system in a continuous process generally speaking like that described above. The oil was heated up to 160°C by means of an extra heating element in the stirring tank 4 under an inert atmosphere of nitrogen. The catalyst was added in the same tank.

324 g of Ni catalyst of type Pricat 9910 with 20 % Ni was used as the catalyst. The quantity corresponds to 0.04 % Ni in the oil which is the normal catalyst quantity when hardening soya oil in a batch reactor. The supply of hydrogen was 3 x 44 Nl/min. and the pressure in the pipe loop was 8 bar.

The test was carried out over 45 minutes. The mean oil flow was 3.8 kg/min. and the mean dwell time for the oil in the pipe batch was 7 minutes.

The so-called iodine value (IV) before hardening was measured at 129 and after hardening at 59.7, i.e. a difference of approximately 70  $\Delta$ IV.

With a mean dwell time of 7 minutes this produces a reaction speed of approximately 10  $\Delta$ IV/min. Compared with the best conventional systems this represents a reaction speed 5-6 times faster.

However, with the present invention not only is the efficiency improved but also important conditions such as considerably lower investment costs, better and more precise process control, lower energy consumption, simpler and more cost-effective operation, lower catalyst consumption, regular hydrogen consumption and the possibility of obtaining better product quality.

Claims

1. A method for hydrogenating oil, fat or fatty acids by adding hydrogen and using a catalyst,  
c h a r a c t e r i s e d   b y  
a semi-continuous or continuous process in which the catalyst is mixed with preheated fat or oil in a mixing device (9/10, 24), the mixture is fed through a preferably serpentine-like, vertically-mounted pipe loop or one or more static mixers (11, 28) where the hydrogen and, possibly, the inert gas is/are added, so that a turbulent co-current is produced, the mixture is cooled during hydrogenation and, alternatively, the oil, catalyst, inert gas and excess hydrogen gas are recirculated after the hardening process.
2. A procedure in accordance with claim 1,  
c h a r a c t e r i s e d   i n   t h a t  
hydrogen and inert gas are added in desired quantities at several points in the pipe loop (11) or in several static mixers (28).
3. A procedure in accordance with claims 1 and 2,  
c h a r a c t e r i s e d   i n   t h a t  
the inert gas is nitrogen.
4. Process equipment for hardening oil, fat and fatty acids,  
c h a r a c t e r i s e d   b y  
feed and mixing devices (A) for supplying and mixing the oil and a catalyst, a preferably serpentine-like, vertically-mounted pipe loop, or one or more static mixers and cooling devices with supply devices for hydrogen gas and, alternatively, inert gas (B), as well as devices (C) for collecting

the oil, separating and recirculating any inert gas and supplying, separating and, alternatively, recirculating used hydrogen gas, as well as possible separation and recirculation of the catalyst.

5. Process equipment in accordance with claim 4, characterised in that the mixing and feed devices (A) comprise a container or autoclave (24), with a base stirrer (25), where the oil and the catalyst are mixed in the autoclave in batches and are fed on to the serpentine-like pipe loop or static mixer(s) (28) by means of a pump (20) via a pipe (27)
6. Process equipment in accordance with claim 5, characterised in that the mixture of oil and catalyst and, possibly, gas is fed from the mixer(s) (28) back to the autoclave (24) through a pipe (37), preferably via a diffuser (20) arranged at the top of the autoclave (24).
7. Process equipment in accordance with claim 4, characterised in that the mixing and feed devices (A) comprise a first pipe system (8) in which are connected a heat exchanger (3) for heating the oil, a holding tank with a stirring device (5) for stirring the oil and a pump (6) for feeding and portioning out the oil, and a second pipe system (9) with a pump (7) for feeding the catalyst from a holding and stirring tank (1, 2), and a mixing device (10) to which the pipe systems (8, 9) are connected and which are arranged immediately before the serpentine-like pipe loop or static mixer(s) (11).

8. Process equipment in accordance with claims 4-6, characterised in that hydrogen gas and inert gas are added to the serpentine-like pipe loop or static mixer(s) (11, 28) in a mixture or separately at several points.
9. Process equipment in accordance with claims 4-8, characterised in that one or more heat exchangers (21, 28) is/are arranged in the pipe loop or static mixer(s) (11).
10. Process equipment in accordance with claims 4 and 7, characterised in that the mixture of oil, catalyst and gas is fed, after the pipe loop or static mixer(s) (11), into a collection tank (16) with a stirring device (12).
11. Process equipment in accordance with the above claims 4-10, characterised in that the gas which is separated in the collection tank (16, 24) is extracted by means of a compressor and is circulated back to the pipe loop or static mixer(s) (11, 28) via a third pipe system (18, 31).
12. Process equipment in accordance with the above claims 4-11, characterised in that the catalyst is separated from the oil by means of a separator, a filter or similar and is fed back to the holding tank (1) via a fourth pipe system (20, 25) or pipe (36).

Fig. 1

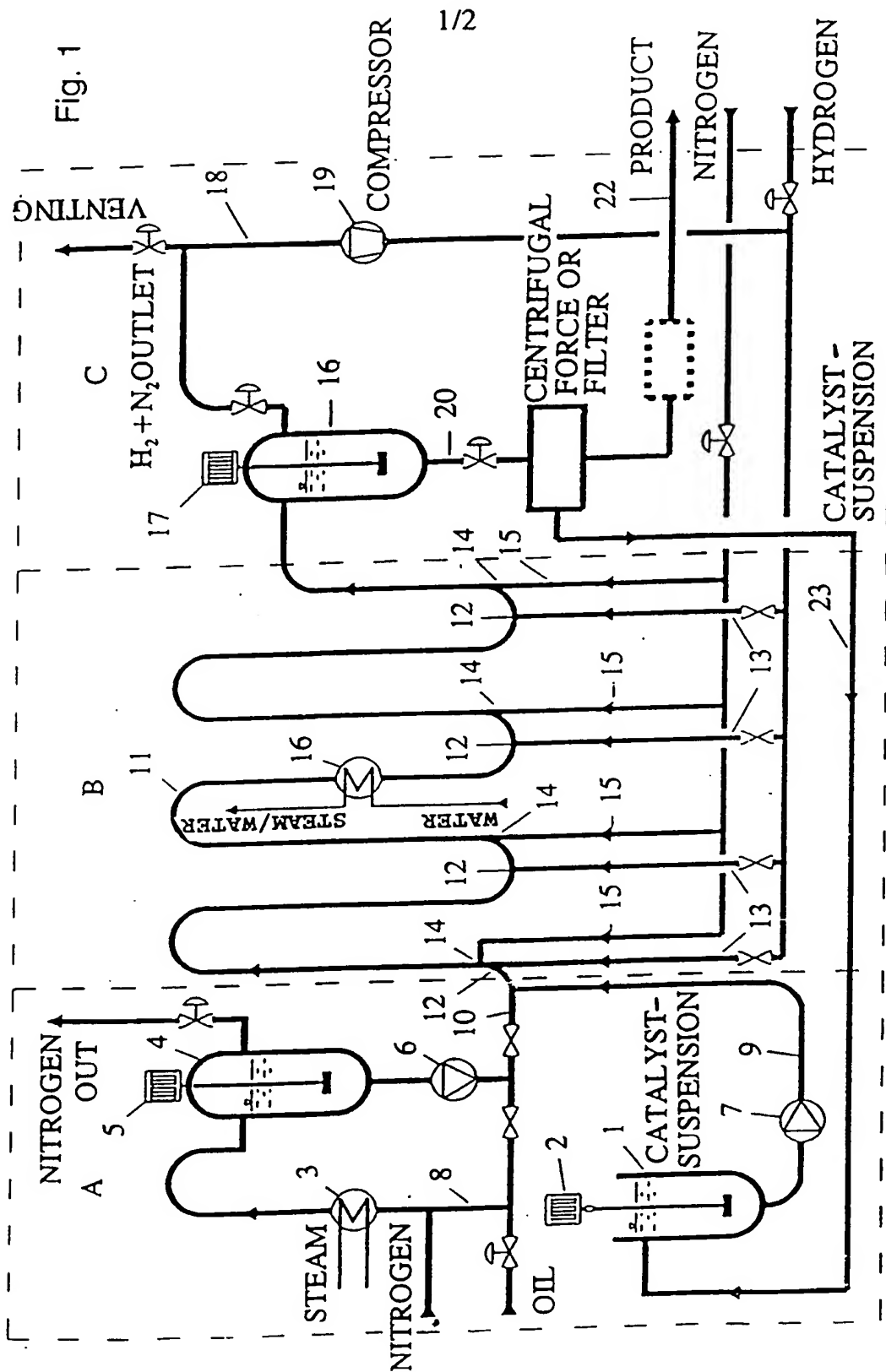
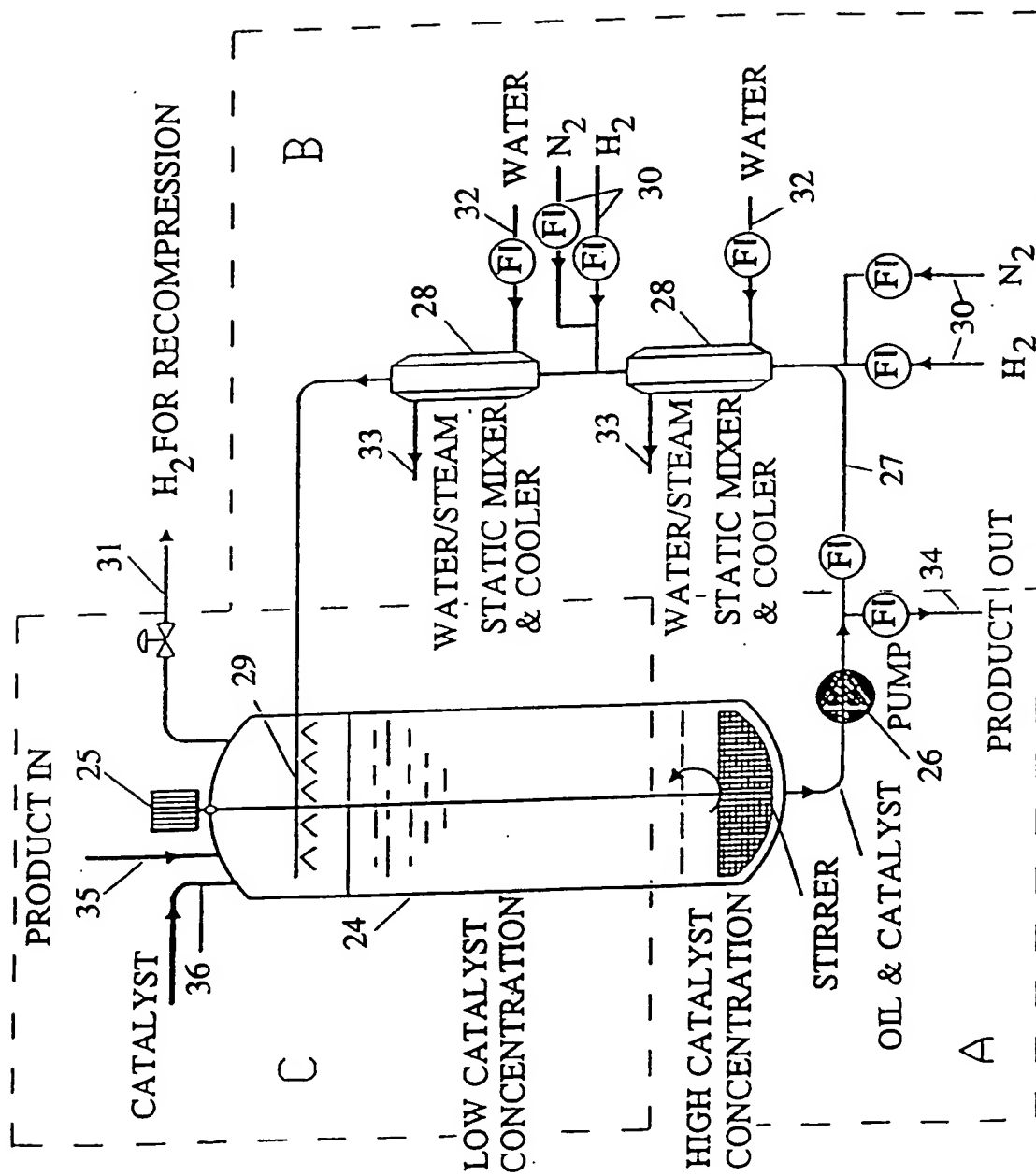


Fig. 2



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 93/00167

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C11C 3/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C11C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CA

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE, B2, 1667316 (UNILEVER N.V.), 16 June 1971 (16.06.71), see the claim; column 4, lines 9 - 49 --	1-7
X	US, A, 3823172 (G.M. LEUTERITZ), 9 July 1974 (09.07.74), see the claim; column 3, line 39 - column 4, line 1-10 --	1-7
X	Derwent's abstract, No 89-164153/22, week 8922, ABSTRACT OF SU, A, 1440908 (KHARK FATS RES INST), 30 November 1988 (30.11.88) --	1-7
A	GB, A, 1107660 (METALLGESELLSCHAFT AKTIENGESELLSCHAFT), 27 March 1968 (27.03.68) --	1-7



Further documents are listed in the continuation of Box C.



See patent family annex.

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## INTERNATIONAL SEARCH REPORT

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4847016 (GERD GÖBEL), 11 July 1989 (11.07.89)  --	1-7
A	US, A, 3792067 (W.A. COOMBES ET AL.), 12 February 1974 (12.02.74)  -- -----	1-7

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

28/01/94

International application No.

PCT/NO 93/00167

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-B2- 1667316	16/06/71	BE-A- 702051 FR-A- 1545667 GB-A- 1167955 LU-A- 54201 NL-A- 6610611	29/01/68 00/00/00 22/10/69 21/05/69 25/01/67
US-A- 3823172	09/07/74	DE-A, B, C 1906448 FR-A- 2004687 GB-A- 1264655 AU-A- 4237672	13/11/69 28/11/69 23/02/72 20/12/73
GB-A- 1107660	27/03/68	BE-A- 690507 CH-A- 478229 DE-A- 1467529 FR-A- 1515060 NL-A- 6616841 US-A- 3444221	02/05/67 15/09/69 16/01/69 00/00/00 05/06/67 13/05/69
US-A- 4847016	11/07/89	DE-A- 3602525 DE-A- 3779665 EP-A, B- 0230971	30/07/87 16/07/92 05/08/87
US-A- 3792067	12/02/74	CA-A- 961051 DE-A, C- 2207909 GB-A- 1390381	14/01/75 07/09/72 09/04/75